

**Experiment title:**Role of Hydrogen Bonding in the High Frequency Dynamics of CH₄, CH₃OH, NH₃, H₂O and HF**Experiment number:**

HS-1166

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Report:

We studied the inelastic x-ray scattering of liquid HF, kept at 273 K in a custom-made cell, in the momentum transfer (Q) range 1-30 nm⁻¹. This work is part of our long-term effort on studying the high frequency collective dynamics of hydrogen bonded liquids.

The HF molecule is known to make a single hydrogen bond which may lead to the formation of small chains of HF molecules and eventually, at low temperatures, to their polymerization. This bond is expected to be substantially stronger than in liquid water. The aim of the present study is to assess the detailed shape of the dynamic structure factor, $S(Q, E)$, of liquid HF at momentum transfers in the surrounding of the inverse of the inter-molecular average distance. The interest, in fact, is to investigate whether this liquid shows characteristic relaxation processes as those discovered in water in the momentum transfer range considered here [1]. As in water, in fact, one may expect to observe the phenomenon of fast sound, associated with the structural relaxation of the making and breaking of the hydrogen bond network characteristic of this liquid. Similarly to liquid water, there is also in HF a large difference between the isothermal sound velocity, c_o , characterizing the low frequency sound propagation, and c_{oo} , the infinite sound velocity expected in the infinite frequency limit, i. e. at frequencies well above the inverse of any characteristic relaxation time of the investigated liquid. Low frequency measurements give $c_o \sim 500$ m/s while numerical simulations [2] predict for c_{oo} values in excess of 3000 m/s, i.e. the ratio c_{oo} / c_o is of the order of 6 while in liquid water is of the order of 2.5.

We report in Fig. 1 a sample of the measured spectra. At variance with the water case, these spectra show a single peak centered around zero energy transfer and no distinct inelastic features. This peak shows, however, a strong Q -dependence becoming increasingly broader with increasing Q , and then narrower in the region around 25 nm⁻¹ where one also finds the first sharp diffraction peak (*FSDP*) in the static structure factor. This behavior, very different from liquid water, has a striking resemblance to a neon fluid measured at similar temperature and density [3]. To allow for a quantitative analysis, the spectra have been fitted using a model for the dynamic structure factor based on the memory function formalism in the infinite frequency limit, i. e.

retrieving a simple fitting function composed by a delta for the central line and a damped harmonic oscillator for the inelastic signal. The model, after convolution with the experimental resolution function gives the best fits superimposed in Fig. 1 to the data. From this first fitting procedure, we obtain the dispersion relation reported in Fig. 2, which shows a linear dispersion in the small Q limit, and a characteristic maximum followed by a minimum at $Q = Q_{F DSP}$. In the small Q -limit the dispersion relation gives a speed of sound of 630 m/s, a value which is somewhat larger than $c_0=500$ m/s, but is sensibly smaller than c_{00} , which approaches 4000 m/s at small Q . This is further emphasized in Fig. 3, where we report the apparent velocity of sound obtained from the dispersion relation of Fig.2 as the ratio $\Omega(Q)/Q$ and the values of c_0 and c_{00} .

In summary, the measured data show striking differences between the high frequency collective dynamics of HF and H_2O while they suggest strong similarities between those of HF and Ne. Further analysis is going on and further experimental work is highly needed to better understand the observed trends. In particular, we should study HF at different temperatures to assess whether the relaxation process is hidden in the present work by structural effects (bending down of the dispersion relation), and, most importantly, we must investigate $(HF)_x(H_2O)_{1-x}$ mixtures as a function of x to determine the evolution of the collective dynamics from the phenomenology of one liquid to that of the other.

- [1] A. Cunsolo, et al., Phys. Rev. Lett. 82, 779 (1999).
 [2] D. Bertolini et al., Phys. Rev. Lett. 81, 2080 (1998).
 [3] A. Cunsolo et al., Phys. Rev. Lett. 80, 3515 (1998).

